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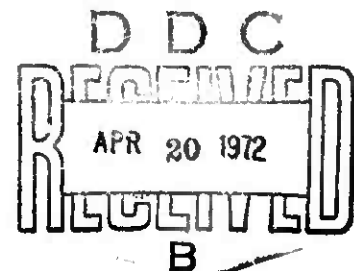
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University of Massachusetts  
Department of Mechanical & Aerospace Engineering  
Amherst, Massachusetts

Preliminary Experiments on the Gas-Phase Ignition Mechanism of  
Ammonium Perchlorate

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PRELIMINARY EXPERIMENTS ON THE GAS-PHASE IGNITION MECHANISM OF  
AMMONIUM PERCHLORATE

Karl Jakus, University of Massachusetts

AROD Grant No. DA-ARO-31-124-71-G97

Abstract

The results of the sublimation experiments that were performed under the AROD Grant No. DA-ARO-31-124-71-G97 and which were intended to be preparatory to the study of the gas-phase ignition mechanisms of Ammonium Perchlorate(A-P) are summarized in this report. These experiments were comprised of the study of the deposition rates from sublimating A-P as function of sublimation temperature; and the comparison of the mass spectra of the sublimating reagent grade A-P with that of already sublimed A-P. The results reinforce the previously reported observations that decomposition competes with sublimation in the temperature range of 100°C to 200°C. Furthermore, the results also indicate that the sublimed A-P is less stable than the reagent grade A-P although the sublimation mass spectra from the two preparations are nearly indistinguishable.

### FINAL REPORT

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Period Covered: 1 March 1971 - 31 August 1971

Title of Proposal: Study of Gas Phase Ignition Mechanisms with Skimming  
Transient Mass Spectrometry

Grant Number: DA-ARO-D-31-124-71-G97

Name of Institution: The Johns Hopkins University

Author of Report: Karl Jakus

Scientific Personnel Supported by this Project:

1. Dr. Karl Jakus  
Principal Investigator  
1 March 1971 - 30 June 1971 : 25%  
1 July 1971 - 31 August 1971: 100%
2. Stephen J. Thompson  
Undergraduate at J.H.U.  
410 hrs @ 2.50/hr.
3. Oliver Engel  
Undergraduate at J.H.U.  
86.5 hrs @ 2.50/hr.
4. Linda A. Ciotola  
Undergraduate at J.H.U.  
152 hrs @ 2.50/hr.
5. David R. Feineman  
Undergraduate at J.H.U.  
27 hrs @ 2.25/hr

Equipment Purchased  
by this Project:

Bendix Model No. MA-3 Mass Spectroscope,  
Serial No. S-12928  
Total Cost: \$11,933.99

PRELIMINARY EXPERIMENTS ON THE GAS-PHASE IGNITION MECHANISM OF  
AMMONIUM PERCHLORATE

Karl Jakus, University of Massachusetts

In May of 1971 Grant No. DA-AR0-31-124-71-G97 was awarded by the Department of Army to the Johns Hopkins University to study the gas phase ignition mechanisms of solid propellant oxydizers such as Ammonium Perchlorate (henceforth referred to as A-P). The primary goal of the research was charted to be the evaluation of the proposed "transient mass spectroscopy" in prospective of relevant propellant systems. Accordingly, the necessary apparatus has been constructed, a mass spectroscope has been selected, purchased and its performance in transient applications has been evaluated.

The technique under consideration entails the rapid vaporization in vacuum of a small sample of solid propellant to form an unsteadily expanding and simultaneously reacting gas cloud with an initial pressure and temperature corresponding to those likely to be encountered during actual propellant combustion. This gas cloud is then "skimmed" with a hypersonic orifice for mass spectroscopic analysis in a fashion similar to high pressure sampling. Previous theoretical<sup>1</sup> and experimental<sup>2,3</sup> work on unsteady expansion of gas clouds as well as the extensive work on steady supersonic expansions<sup>4</sup> serve as a foundation for the technique. The kind of flow field the "skimmer" orifice would experience in such an expansion process is illustrated in Figure 1 where the number flux and flow velocity in an expanding silver cloud are plotted against time.<sup>3</sup> It is interesting to note that while the initial cloud density was approximately  $5 \times 10^{17}$  atoms/cm<sup>3</sup> the density at the peak of the curve is only  $1.5 \times 10^{15}$  atoms/cm<sup>3</sup> which represents, under isentropic conditions, a reduction in collision rate of  $5 \times 10^{-4}$ .

Such drastic reduction in collision rates may indeed be used to "freeze" the chemical reactions at various stages of development in a propellant gas cloud.

In the experimental program the gas phase decomposition of A-P was chosen as the first chemical system to be studied with the above "skimming" mass spectrometry. It was proposed that small samples of A-P would be deposited by sublimation on metallic filaments and subsequently, these samples would be vaporized rapidly by ohmic heating the filament. The preparation of these samples are essential to the study of the gas phase chemistry, consequently considerable attention has been devoted to the sublimation characteristics of A-P. The remainder of this report summarizes the results related to the sublimation portion of the program.

Two kinds of sublimation experiments were performed on A-P. First, the deposition rate of A-P onto a "filament" was measured and second, mass spectra were obtained from sublimating samples of reagent grade A-P as well as from samples of A-P that were collected as sublimate in previous experiments. Figure 2 shows the A-P deposition thicknesses as function of time and temperature that were obtained in vacuum on a 0.632" diameter nichrome wire. In the study related to the mass spectra, the sublimation and decomposition products emerging from a pyrex oven in vacuum were allowed to enter directly into the ionization chamber of a Bendix MA-3 time-of-flight mass spectroscope. The arrangement of the apparatus resembled those constructed by previous experimenters<sup>5,6</sup>. Figure 3 shows, as function of temperature, the relative abundance of the predominant species present during the sublimation of reagent grade and sublimed A-P samples. Both of the samples exhibit an increase in the relative concentration of the decomposition products -  $O_2$ ,  $Cl_2$ ,  $NO_2$  - and a decrease in the sublimation products

-  $\text{HClO}_4$ ,  $\text{NH}_3$  - as the temperature increases from  $100^\circ$  to  $200^\circ$  C. Thus the previously reported observation that decomposition competes with sublimation at low temperatures is reinforced by the above results. Some differences exist, however, between the spectra of the two different A-P samples. Decomposition seems to overtake sublimation at a considerably lower temperature in the case of the sublimed A-P than it does in the case of the reagent grade A-P. This characteristic of the sublimed A-P corresponds to its previously reported<sup>7</sup> shorter induction period. The following observations may be made concerning the results which are not illustrated on Figure 3. Both samples produced a spectrum in which the peaks 84 ( $\text{HClO}_3$ ), 67 ( $\text{ClO}_2$ ) and 51 ( $\text{ClO}$ ) followed the parent peak of 100 ( $\text{NClO}_4$ ) indicating that they, in fact, are ionization fragments of the perchloric acid. Furthermore, the peak 30 ( $\text{NO}$ ) approximately followed the peak 46 ( $\text{NO}_2$ ) as it was expected since  $\text{NO}$  is an ionization fragment of  $\text{NO}_2$ <sup>8</sup>. Figure 4 compares the concentration of  $\text{O}_2$  (a decomposition product) and of  $\text{HClO}_4$  (a sublimation product) of the herein discussed two samples with that of the experiments of Heath and Majer<sup>5</sup>. It is apparent from the graphs that Heath and Majer's results show marked similarity to the results obtained with the sublimed A-P sample. Figure 5 illustrates that, although the sublimed A-P sublimates itself its spectra show striking resemblance to the spectra of the decomposition products obtained in the event when all of the reagent grade A-P sample has vaporized out of the oven.

From the above results one may conclude that it is possible to deposit by sublimation small samples of A-P on "filaments" such that the chemical behavior of the sublimed A-P would be similar to A-P prepared by other methods although the sublimed compound seems to be relatively less stable.

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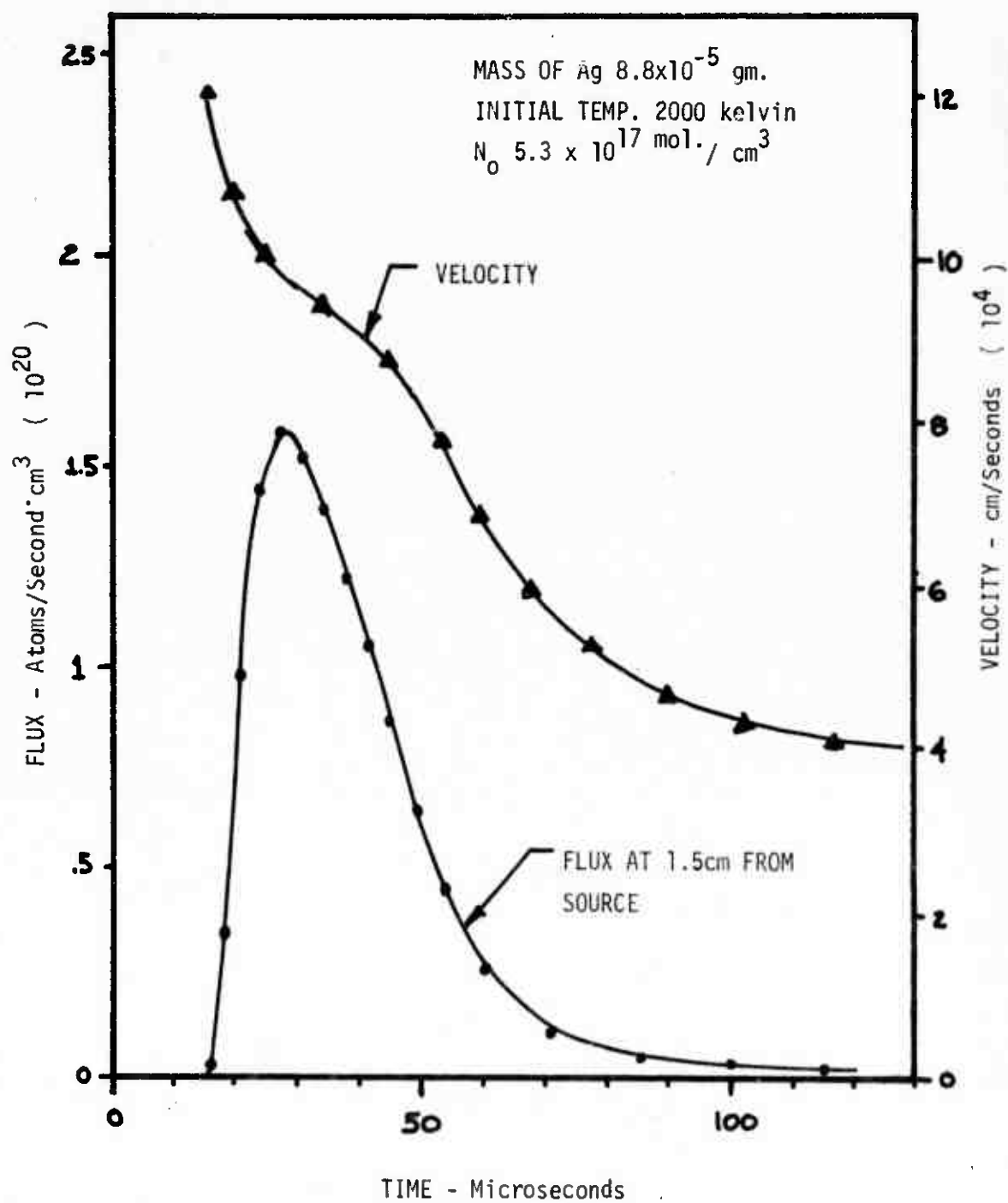


Figure 1. Aerodynamic Expansion of Silver Vapor (From Reference 3.)

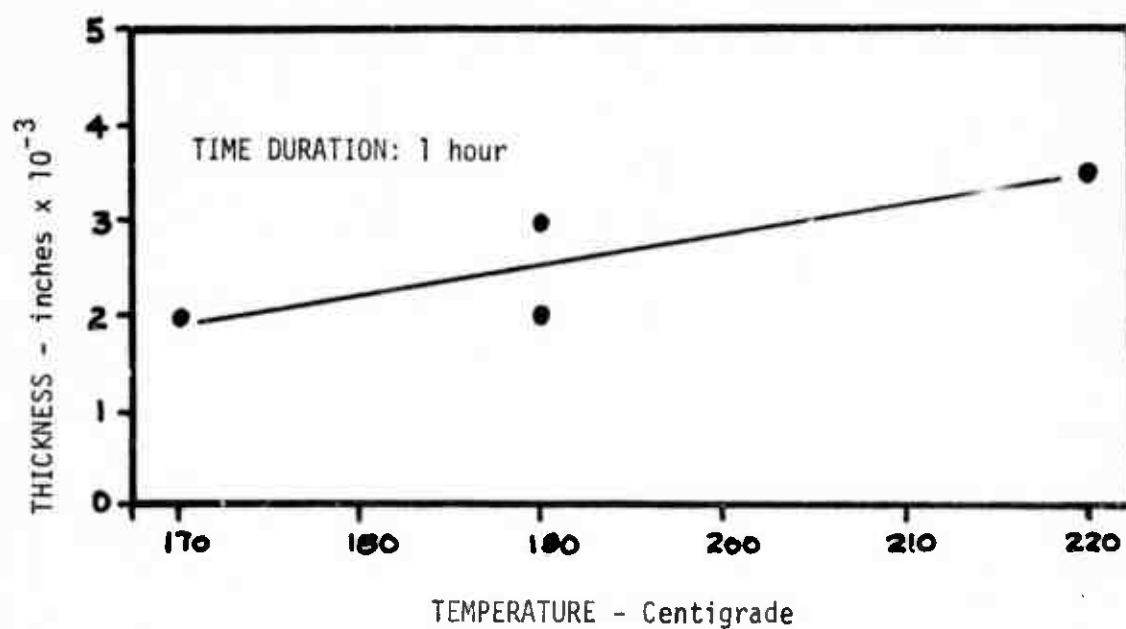
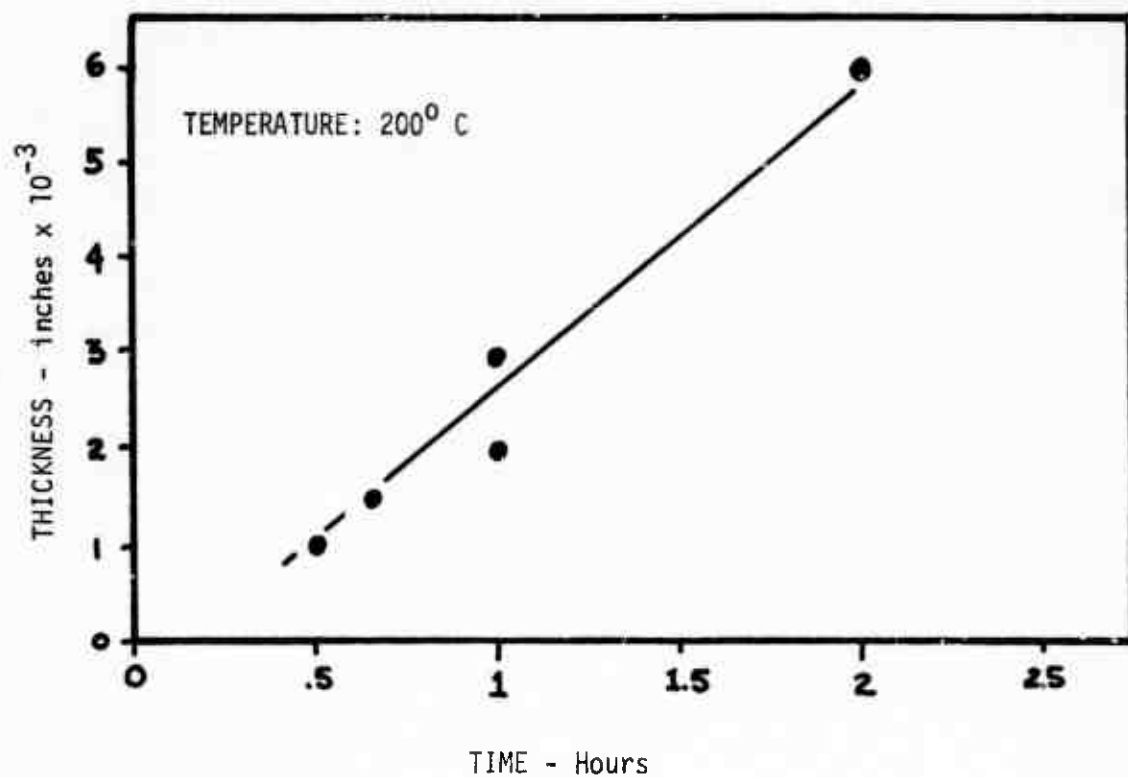


Figure 2. Deposition of A-P onto a 0.032 inches Diameter Wire by Sublimation.

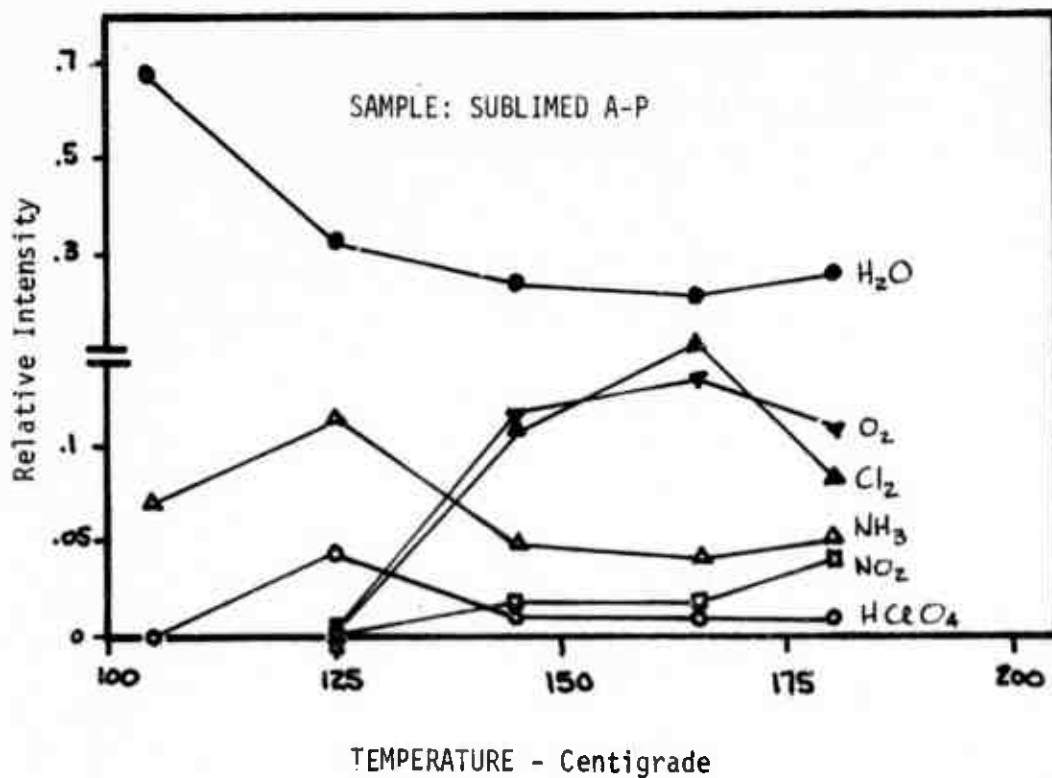
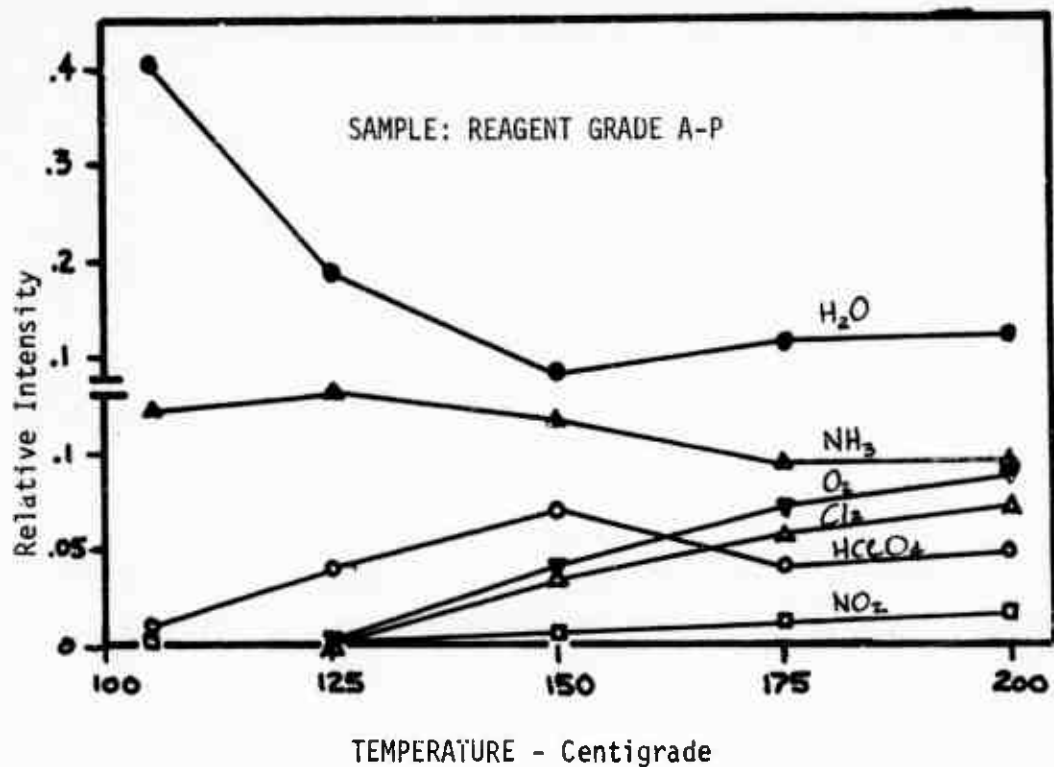


Figure 3. Relative Concentration of the Major Sublimation and Decomposition Products of A-P.

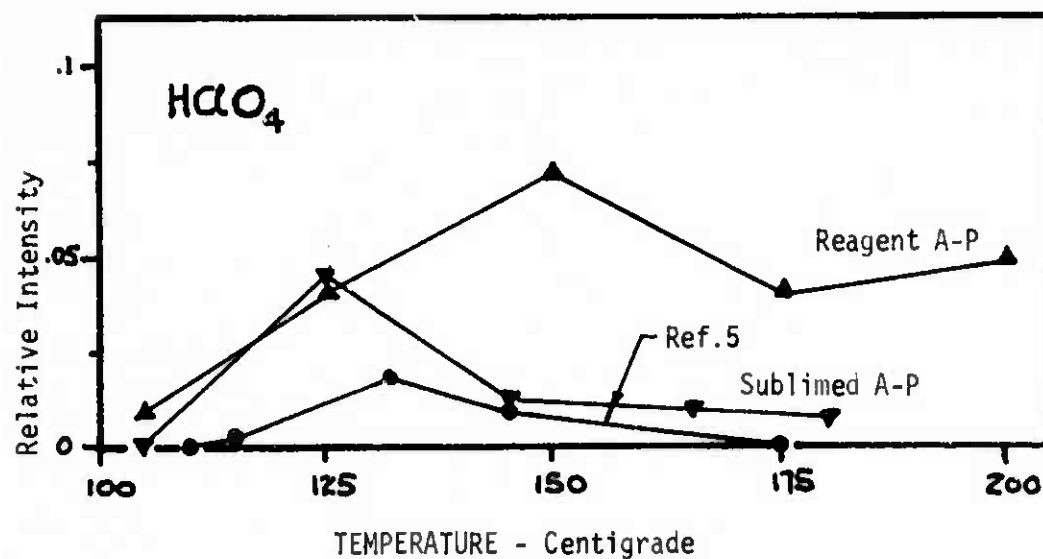
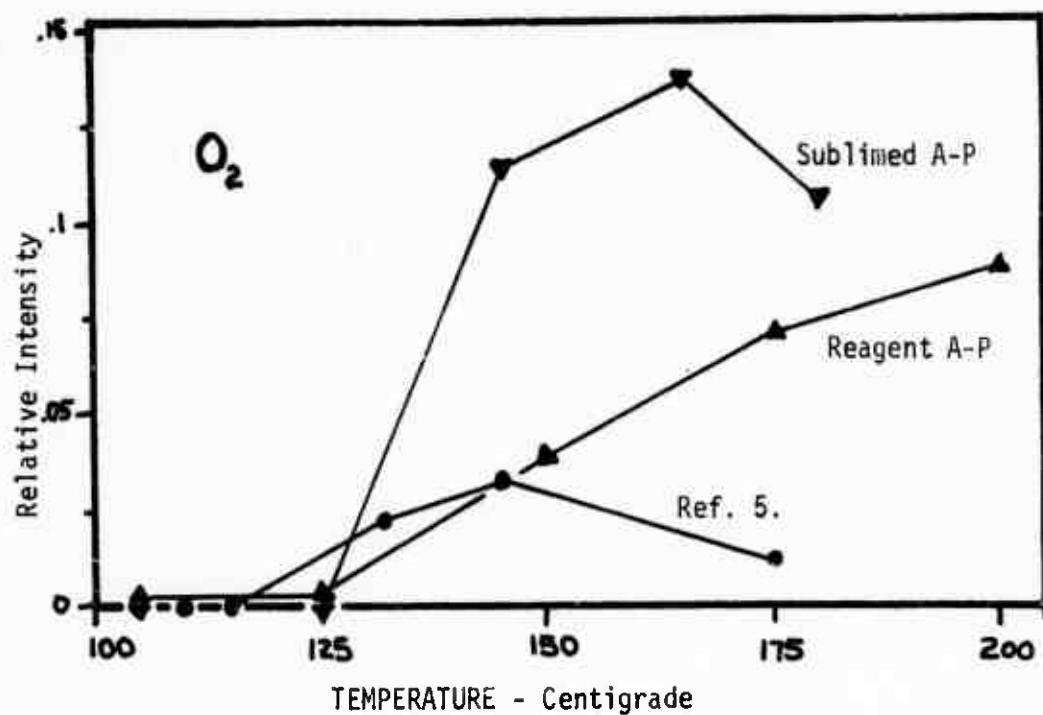
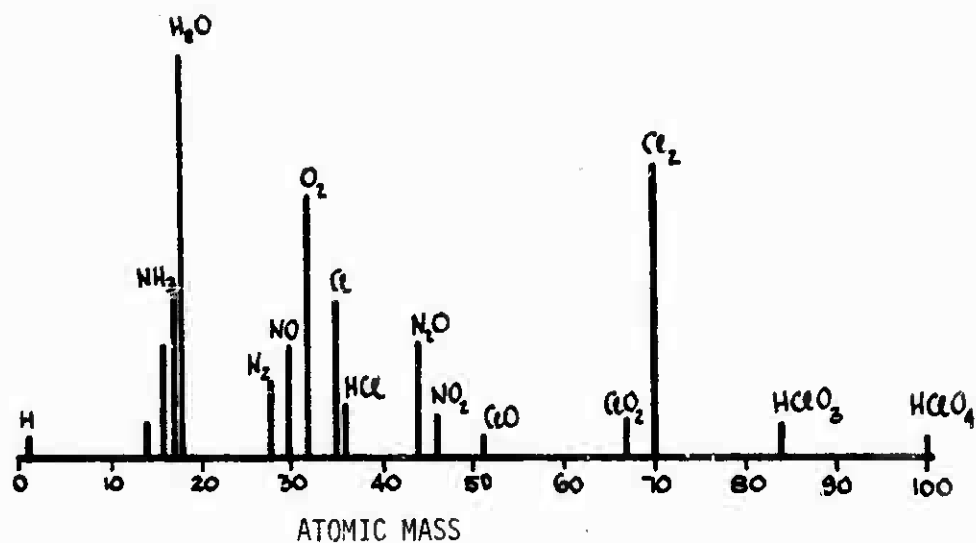
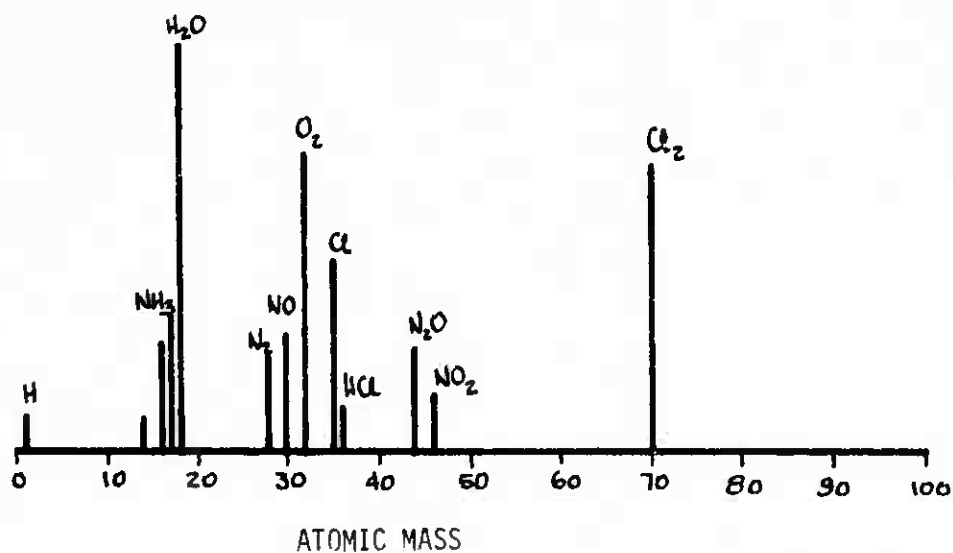


Figure 4. Relative Concentration of  $O_2$  and of  $HClO_4$  in the Mass Spectra of A-P.



SAMPLE: SUBLIMED A-P AT 165° C



SAMPLE: GASEOUS RESIDUE FROM REAGENT GRADE A-P AT 150°

Figure 5. Mass Spectra of Sublimed and Reagent Grade A-P Samples